


Lanthanides | Hot Paper |

 **Ln₃Q₉ as a Molecular Framework for Ion-Size-Driven Assembly of Heterolanthanide (Nd, Er, Yb) Multiple Near-Infrared Emitters**Flavia Artizzu,^{*[a, b]} Francesco Quochi,^[b] Luciano Marchiò,^[c] Raquel Fonseca Correia,^[a] Michele Saba,^[b] Angela Serpe,^[a] Andrea Mura,^[b] Maria Laura Mercuri,^[a] Giovanni Bongiovanni,^[b] and Paola Deplano^{*[a]}

Abstract: A unique example of discrete molecular entity Nd_yEr_xYb_{3-(x+y)}Q₉ (**1**) (Q = quinolinolato) containing three different lanthanides simultaneously emitting in three different spectral regions in the NIR, ranging from 900 to 1600 nm, has been synthesized and fully characterized. A simple molecular strategy based on tuning metal composition in the Ln₃Q₉ framework, which contains inequivalent central and terminal coordination sites, has allowed a satisfactory ion-size-driven control of molecular speciation close to 90%. In **1** the central position of the larger Nd ion is well distinguished from the terminal ones of the smaller Yb³⁺ and Er³⁺, which are almost “vicariants” as found in the heterobimetallic Er_xYb_{3-x}Q₉ (**2**). The Ln₃Q₉ molecular architecture, which allows communication between the ions, has proved to afford multiple NIR emission in **1** and **2**, and is promising to develop a variety of multifunctional materials through the variation of the Ln composition.

Lanthanide ions play a crucial role in modern technology due to their very peculiar luminescent and magnetic properties related to the nature of their 4f core-like electrons.^[1] Heterometallic coordination compounds containing two or more different lanthanide cations are therefore attractive as they can lead to multifunctional materials in which different physical properties can be combined in the same architecture and enhanced properties may be achieved through intermetallic communication.^[2,3]

However, the design of polymetallic lanthanide compounds with well-defined and easily reproducible structures is a challenge, and fully characterized mixed-lanthanide coordination compounds still represent very rare examples in the literature. Among them, heteropolymetallic metal-organic frameworks and coordination polymers, have been very recently proposed as near-infrared- or visible-luminescent barcodes.^[4] In such compounds, different lanthanide ions are randomly distributed over the coordination network, thanks to the similarity of ionic radii and chemical behavior, and their emission properties are simultaneously displayed. However, little control can be achieved on the distribution and distances between the different metals resulting in “diluted” materials in which independent physical properties carried by different Ln³⁺ are superimposed. Instead, to ensure efficient intermetallic communication, the distance between the lanthanide ions and their relative positions should be controlled.^[2b,3,5] In addition, for application purposes, functional materials that can be easily processed without altering their properties through convenient, easy-to-handle, solution methods^[6] or by techniques commonly used for the fabrication of technological devices, such as vacuum deposition, are strongly desirable. In this context, discrete polynuclear molecules in which Ln³⁺ ions are connected through bridging atoms, could fit all these requirements much more easily than multidimensional coordination networks or suspensions/solutions of aggregates/clusters or even larger and heavy polymetallic assemblies.^[4,7,8]


We present here a simple molecular strategy for achieving effective interplay of optical properties of near-infrared (NIR) luminescent functional materials by mixing Yb³⁺, Er³⁺, and Nd³⁺ in heterometallic trinuclear lanthanide quinolinolato (Q) complexes of general formula Ln₃Q₉, a class of coordination compounds that have been investigated for use as active centers into optical silica fiber amplifiers and are also of interest in view of their magnetic properties.^[9,10] In these luminophores, the Q ligand is particularly efficient as light-harvesting “antenna” for all the NIR lanthanide emitters (Er³⁺, Yb³⁺, Nd³⁺), thanks to resonance energy transfer (RET) to lanthanide ion’s higher levels (sensitized emission), to overcome the very small absorption coefficients of the lanthanide-based line-like parity-forbidden intrashell transitions.^[10,11]

The heterotrimetallic Nd_yEr_xYb_{3-(x+y)}Q₉ (**1**) and the heterobimetallic Er_xYb_{3-x}Q₉ (**2**) complexes, were obtained by using a mixture of salts of the selected NIR emitting lanthanide ions, Er³⁺, Yb³⁺, and Nd³⁺, and the ligand in the suitable molar

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ratios through a one-pot reaction optimized for Ln_3Q_9 complexes ($\text{Ln} = \text{Er},^{[10a]} \text{Yb},^{[3]} \text{Gd}^{[11a]}$). X-ray results on single crystals, supported also by powder-XRD experiments (see Supporting Information), show that **1** and **2** are both isostructural with the analogous trinuclear Er_3Q_9 complex.^[10a] The molecular structure of **1** is chosen here as representative and reported in Figure 1, whereas structural data for **2** can be found in the Supporting Information.

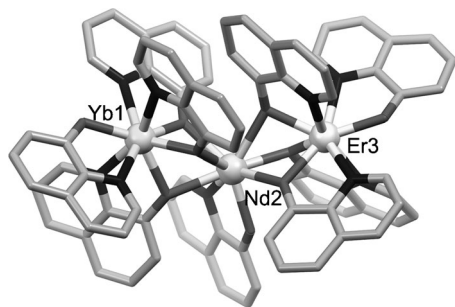


Figure 1. Molecular structure of **1**. Hydrogen atoms were removed for clarity.

In the homoleptic Ln_3Q_9 molecules, the central and terminal coordination sites are inequivalent, and the two outer metals have a N_4O_4 coordination environment, while the inner one has a NO_7 environment. X-ray structural refinement parameters for **1** (Table S4 in the Supporting Information), allow for a reliable attribution of the central position to the “light” and larger Nd ion that can be well distinguished from the “heavy” Yb^{3+} and Er^{3+} ions, which in turn occupy the terminal sites. The intermetallic distances of 3.586 Å for $\text{Ln1}\cdots\text{Nd2}$ and 3.573 Å for $\text{Nd2}\cdots\text{Ln3}$ ($\text{Ln} = \text{Er}, \text{Yb}$) are in this case significantly longer than those determined for **2** (see later) and also for Er_3Q_9 ^[10a] and Yb_3Q_9 ^[10e] in agreement with the differences in ionic radii between these ions. From electron density maps reported in Table S4 (in the Supporting Information) and relative discussion, the best description of this complex is NdErYbQ_9 .

Instead the close similarity of erbium and ytterbium electronic densities hampers a clear discrimination between these two ions by X-ray diffraction and no significant differences in the structure refinement parameters for the different metal occupancies are found for **2** (Table S5 in the Supporting Information). However, intermetallic distances, 3.475 Å for $\text{Ln1}\cdots\text{Ln2}$ and 3.478 Å for $\text{Ln2}\cdots\text{Ln3}$, are slightly shorter than the homonuclear Er_3Q_9 (3.488 and 3.495 Å).^[10a] These geometric considerations, together with analytical data (vide infra), are in support of a mixed metal molecular composition ErYb_2Q_9 , as discussed in detail in the Supporting Information.

It must be remarked that the isostructurality of these trinuclear quinolinolato complexes with Ln ions belonging both to the first and second half of the lanthanide series, is a rare case,^[12] and allows great versatility for mixing, at a molecular level, Ln ions as carriers of different functionalities, without altering the molecular architecture. Moreover, the short intermetallic distances found in **1** and **2**, both between adjacent and also between terminal Ln ions ($\text{Ln1}\cdots\text{Ln3}$ separation is 6.549 Å

for **1** and 6.386 Å for **2**) lie well below the Förster's resonance energy transfer radius R_0 of about 10 Å and are thus optimal to ensure fully efficient intermetallic communication between the NIR-emissive Yb and Er ions.^[3,4]

Due to the close composition–structure–property relationship in these kinds of heterometallic functional molecular materials, the accurate determination of metal composition is crucial for achieving a satisfactory insight into these systems. To this end, ICP-mass analysis on solution samples has proven to be a valuable technique. Metal ratios of Nd:Er:Yb 1:1.14:1.27 were found for **1** after repeated measurements on several independent batches of the compound. A similar trend can be observed for **2** ($\text{Yb}/\text{Er} = 2.36$), hinting to a slightly stronger affinity of Yb^{3+} upon coordination to the 8-quinolinolato ligand, likely connected to its slightly smaller ionic radius compared to Er^{3+} .^[2a] The purity and homogeneity of the compounds have been verified by SEM-EDX semi-quantitative punctual analyses (see Supporting Information) on different single crystals, which have shown reproducible metal atomic ratios close to expected values. Compositional analysis on single molecules has then been done by electrospray (ESI) mass spectrometry experiments in positive ion mode. The ESI-mass spectra, reported in Figure 2, show the presence of peaks related to $[\text{Ln}_3\text{Q}_9]^+$ fragments clearly demonstrating that the trinuclear structure is preserved in solution. The most intense peaks are related to the mixed species, $[\text{NdErYbQ}_9]^+$ ($m/z = 1637.9$, **1**) and $[\text{ErYb}_2\text{Q}_9]^+$ ($m/z = 1666.2$, **2**), confirming the coexistence of the three NIR-emissive lanthanide ions Nd^{3+} , Er^{3+} and Yb^{3+} in the same discrete molecular architecture.

Analysis of the ESI-mass spectrum of **1** (Figure 2, upper panel) provides clear evidence of the presence of one neodymium ion in each single molecule, in agreement with XRD structural data. In the experimental spectrum (curve a), the

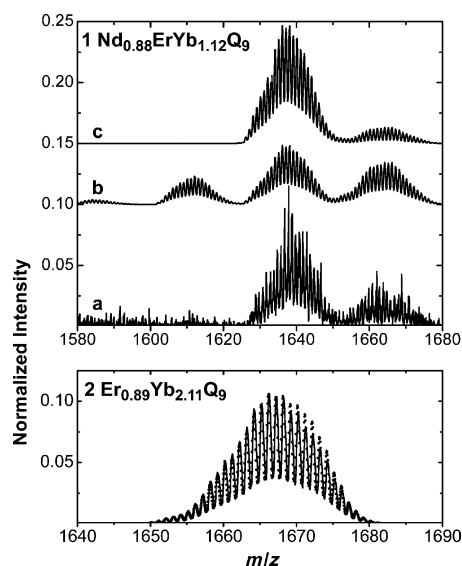


Figure 2. Expanded region of the ES(+) mass spectrum of: **1**, experimental spectrum (a) and model spectra for Nd in a fixed central site (c) and for a statistical metal distribution of Nd, Er and Yb (b) according to atomic ratios retrieved from ICP-mass analysis; **2**, experimental spectrum (black curve) and model spectrum (dots), see text.

most intense peak corresponds to a convolution of isotopic patterns of heterometallic $[\text{NdLn}_2\text{Q}_8]^+$ ($\text{Ln} = \text{Er}, \text{Yb}$) species, while the residual fragments at higher m/z values, related to molecules containing only Yb and Er, are ascribable to the excess of these two ions in the sample, as shown by ICP-mass data. Moreover, no fragments relative to species containing more than one neodymium ion are observed, providing further support to the central molecular site as preferential for the larger Nd^{3+} with respect to the Er^{3+} and Yb^{3+} ions, sitting in the two equivalent peripheral positions. To corroborate these observations, two models for the $\text{Nd}_{0.88}\text{ErYb}_{1.12}\text{Q}_9$ composition, retrieved from ICP-mass analysis, have been compared. Figure 2 (upper panel) clearly points out that, while experimental data significantly differ from a statistical model spectrum obtained for a random and independent metal occupancy over three molecular sites (curve b), they can nonetheless be adequately described (curve c) by applying some constraints, that is, by assuming one Nd^{3+} ion per molecule and statistical occupancies for Yb^{3+} and Er^{3+} over the two remaining sites. These conclusions allow to estimate, for this heterotrimeric system, a molecular speciation of only three predominant configurations: NdErYbQ_9 (ca. 44%), NdYb_2Q_9 (ca. 25%) and NdEr_2Q_9 (ca. 19%). This size-discriminating effect is very relevant here that it leads to relative abundance (ca. 88%) of heterometallic Nd-Ln_2 ($\text{Ln} = \text{Er}, \text{Yb}$; $\Delta r_{\text{Nd-Er}}^{\text{CN}=8} = 10.5$ pm and $\Delta r_{\text{Nd-Yb}}^{\text{CN}=8} = 12.4$ pm) molecules comparable to the best result (90%) found in the literature in the case of one-pot synthetic strategies, for the thermodynamic formation of heterobimetallic La-Lu ($\Delta r_{\text{La-Lu}}^{\text{CN}=8} = 18.3$ pm) triple-stranded helicate.^[13,14] It is worth noting that size selectivity of substituted quinolinolato ligands towards lanthanide ions has been already observed in the case of mononuclear complexes.^[15] The experimental spectrum of **2** can be satisfactorily fitted for $\text{Er}_{0.89}\text{Yb}_{2.11}\text{Q}_9$ composition, on the basis of a statistical occupancy model of erbium and ytterbium ions over the three possible molecular sites (dotted curve, Figure 2, lower panel). This provides further evidence of the analogous chemical behavior of Er^{3+} and Yb^{3+} that can be considered as “vicariants”, on dependence of their very similar ionic radii ($\Delta r_{\text{Er-Yb}}^{\text{CN}=8} = 1.9$ pm).

Optical properties of the complexes have been also investigated to check for the coexistence of multiple emissions due to the presence of the different lanthanide ions. The absorption spectra of **1** and **2**, featuring a broad and intense absorption related to ligand $\pi-\pi^*$ transitions and numerous sharp peaks originated from intrashell f-f transitions of Nd, Er, and Yb ions, are shown in Figure 3 a and b.

Upon ligand excitation in its lowest absorption band, some residual emission in the green ($\lambda_{\text{max}} = 520$ nm) related to ligand fluorescence is detected for both the compounds (Figure 3 c). After resonance energy transfer from ligand excited triplet states to the upper energy levels of the lanthanide ions, photoluminescence at 1 and 1.5 μm , due to $\text{Yb}^{3+} \ ^2\text{F}_{7/2} \rightarrow \ ^2\text{F}_{5/2}$ and $\text{Er}^{3+} \ ^4\text{I}_{13/2} \rightarrow \ ^4\text{I}_{15/2}$ transitions respectively, is simultaneously detected for **2**, as shown in Figure 3 d (blue). In the case of **1**, three emission bands covering almost the entire NIR spectrum from 900 to 1650 nm are observed as a result of the simultaneous excitation and radiative decay of Nd^{3+} ($\ ^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{9/2}$ 890 nm,

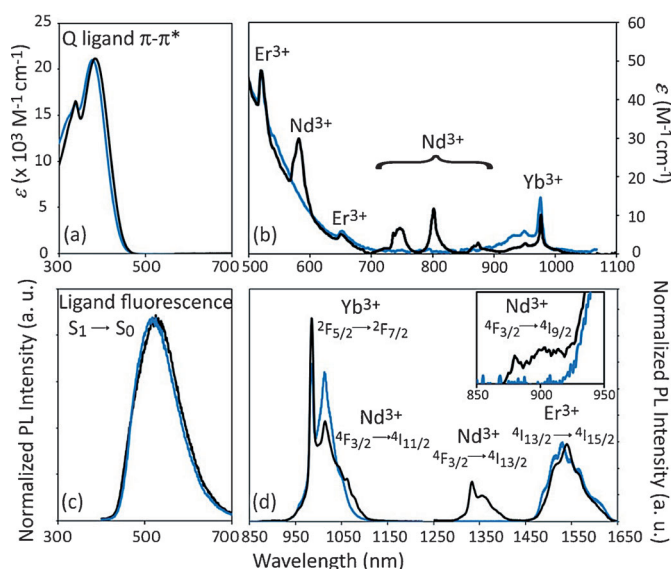


Figure 3. Absorbance spectrum of **1** (black) and **2** (blue) in DMSO solution showing a) the broad band related to the Q ligand in the UV-Vis region and b) lines related to intrashell f-f transitions of Nd^{3+} , Er^{3+} , and Yb^{3+} in the Vis-NIR. c) Ligand fluorescence and d) PL spectra in the NIR region, of DMSO solutions of **1** (black) and **2** (blue) excited at $\lambda = 355$ nm. Spectroscopic labels of Nd^{3+} , Er^{3+} , and Yb^{3+} transitions are also indicated. PL spectra have been normalized for solution absorption at excitation wavelength and laser power.

$\ ^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{11/2}$ 1070 nm, $\ ^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{13/2}$ 1350 nm), Er^{3+} ($\ ^4\text{I}_{13/2} \rightarrow \ ^4\text{I}_{15/2}$ 1540 nm), and Yb^{3+} ($\ ^2\text{F}_{5/2} \rightarrow \ ^2\text{F}_{7/2}$ 980 nm), see Figure 3 d, black curve. Crystal field effects split the energy levels manifolds of the f-states resulting in band broadening and resolution into a fine structure on dependence on the symmetry of the coordination environment around the lanthanide ion. Consequently, Yb and Er emission bands in **1** and **2** display slightly different shapes likely related to the different coordination sites (central and/or peripheral) occupied by these ions in the two samples.

The observed PL spectroscopic features originate from the contribution of the different species in the two samples. However, it is interesting to note that Er emission bands in **1** and **2** are equally intense, suggesting that efficient Yb-Er energy transfer, already demonstrated for the bimetallic Yb-Er case,^[3] takes place similarly in the trimetallic complex. The observed Yb^{3+} residual emission can be ascribed to the fraction of molecules not containing erbium, although, in **1**, other phenomena such as Nd to Yb energy transfer, currently under investigation, cannot be ruled out. These features make **1** a potential broad-band NIR emitter for which the intensities of the three different main emissions can be finely tuned on varying metal composition and hence molecular speciation.

In conclusion, we have synthesized and fully characterized two heterometallic complexes of NIR emitting lanthanide ions, with a trinuclear structure of general formula Ln_3Q_9 . Complex **1** represents, to the best of our knowledge, the first example of a discrete molecular unit containing three different NIR-luminescent lanthanide ions, Nd^{3+} , Er^{3+} , and Yb^{3+} , simultaneously emitting upon ligand excitation at a single wavelength.

From results obtained from XRD structural studies, EDX and ICP-mass analyses, and ESI-mass spectrometry, it can be deduced that the lighter and larger Nd³⁺ ion can be chemically discriminated from the heavier and almost "vicariants" Er³⁺ and Yb³⁺ and helps in controlling molecular speciation and metal distribution across the coordination sites in polynuclear discrete molecules, in which the metals sit at short distances from each other. This would be particularly useful for achieving controlled intermetallic communication and tunability of physical properties in solution-processable functional molecular materials through a rational and easy-to-handle synthetic strategy simply by controlling reactant stoichiometry. Studies on the energy-transfer mechanisms between the different NIR-emitting lanthanide ions are currently being performed in our laboratories as well as the investigation of their processing potential through mild solution techniques in order to explore potential applications as doped optical waveguides and amplifiers.

As final remark, we note that the described molecular strategy provides a powerful tool for obtaining a variety of multifunctional compounds, beyond those for photophysical applications,^[10g] simply on variation of the Ln ions as carriers of functionality.

Experimental Section

Details of the synthesis and characterization of **1** and **2** can be found in the Supporting Information. CCDC 1026425 (**1**) and 1026426 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: heterometallic complexes • lanthanides • luminescence • multifunctional materials • structure elucidation

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